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STRUCTURE AND PROPERTIES OF COMPOSITE MATERIALS FOR MEDICAL APPLICATION

A. Yu. Malysheva,¹ B. I. Beletskii,¹ and E. B. Vlasova¹

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The main types of composite materials for medical application are considered. The effect of the compatibility of components and the production method on the structure and properties of implant materials is investigated. Classical and specific rules for development and studies of medical-purpose composites of the calcium phosphate – glass type are postulated.

Attempts to develop materials for producing medical implants which combine biocompatibility, porosity, and at the same time a certain level of strength parameters causes substantial difficulties. The development of composites consisting of substances of different types makes it possible to develop a material combining properties of coexisting phases (primarily bioactivity and required mechanical properties) and to obtain implants with the required level of technological and service parameters. Being structurally integral materials, the composites in their properties exceed the average or summary properties of individual components and manifest synergism.

¹ D. I. Mendeleev Russian Chemical Engineering University, Moscow, Russia.

Bioactive components in composite materials (CM) for implanting are represented by various calcium phosphates. They are primarily calcium hydroxylapatite (HA) $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ and the low-temperature form of tricalcium phosphate (TCP) $\beta\text{-Ca}_3(\text{PO}_4)_2$, which are the main minerals of bone tissue. They can be fixed on a solid base or be classical composites representing physicomachanical mixtures (Table 1). It is possible to obtain structural materials for making various-shaped implants from them only in the case when the calcium phosphate is fixed to a solid base.

Until recently, insufficient attention was paid to composites with a brittle matrix, but their importance should grow in future. Low-melting glasses hold the highest promise as matrixes for structural CM. Their temperature range makes it

TABLE 1

Disperse (spray-deposited) phase	Matrix	CM type	Production method	Strength, MPa		Elasticity modulus, GPa	Published source
				bending	compressive		
Calcium phosphates	Collagen	Suspension	Mixing	–	–	–	[2]
	Polyamide, methacrylates	Viscoelastic with time-dependent properties	Polymerization or casting	150	55	3.5	[3]
	Titanium, stainless steel	Multilayer coating	Plasma or thermal spray deposition, electrophoresis	–	669	207	[4]
	Al_2O_3 , ZrO_2 , TiO_2	Strengthened by disperse particles	Casting on a thermoplastic binder	196–245	–	–	[5]
	Al_2O_3 , ZrO_2 , Y_2O_3	The same	Directed eutectoid crystallization	–	–	–	[6]–[8]
	TiO_2	Porous powder composite with continuous skeleton	Reaction sintering	110	155	1.0	German Patent No. 3301122
	Aluminoboron-silicate glass	The same	Liquid sintering	4.7–12.6	12.8–18	1.8–5.0	[1]
SiC , Al_2O_3 fiber	Bioactive glass ceramic	Material on brittle matrix reinforced with fiber	Powder sintering	465	1800	148	[9]
Boron-silicate glass fiber	Polypropylene	Material on viscoelastic matrix reinforced with glass fiber	The same	–	–	3.0–3.5	[10]

TABLE 2

Characteristics	Composite materials		
	disperse-hardened	hardened by particles	reinforced with fiber
Matrix role	Supports the main load	Supports part of the load	Transmits the load to fiber
Filler size, quantity, and role	0.01 – 0.10 μm , below 15 vol.%, prevents migration of dislocations	Over 1 μm , over 15 vol.%, intensifies compression of matrix, provides hardening in brittle composites	Length : diameter ratio over 1, 1 – 70 vol.%, supports the main load, prevents migration of dislocations

possible in the course of technological operations to avoid thermal instability or a decline in the biological activity of the filler, which is calcium phosphate.

The physicochemical and thermal compatibility of the filler and the matrix is apparently one of the most essential problems which have to be solved in developing practical compositions. Appropriate adhesion between them is needed to provide for adequate strength and the optimum load distribution, whose mechanism is determined by the type of CM (Table 2) and the method of its production.

The first studies in the field of selecting glass matrixes for calcium phosphate were the ones [1] determining the crystal-chemical and technological properties of glasses which are inert to HA and suitable for the production of sintered CM. The compositions of these glasses are close to the composition of industrially produced medical glass NS-2A in the feldspar – silica system (Table 3).

Factors affecting the strength of CM

<i>Production method</i>	<i>Factor</i>
Eutectoid crystallization	Crystallographic coupling of phases
Coating deposition	Relief, existence of transition layers
Powder method.	Type of phase arrangement: in the form of discrete particles or continuous (skeleton)

The present study attempted to use this glass as the matrix for another variety of calcium phosphate, i.e., the low-temperature form of tricalcium phosphate $\beta\text{-Ca}_3(\text{PO}_4)_2$ (Table 4). However, the introduction of $\beta\text{-TCP}$ in the amount of 10% (here and elsewhere mass content is indicated, unless otherwise specified) causes intense crystallization of glass with the formation of SiO_2 modifications and shifts the sintered state region beyond 950°C , at which temperature the material loses its bioactive properties, whereas HA could be introduced up to 60% at temperatures $740 - 800^\circ\text{C}$. This is apparently due to the significant difference in the surface energies of HA and $\beta\text{-TCP}$ crystals, which have different basicity and surface hydration. The more complete wetting and the presence of a diffusion barrier in the form of emerging glass crystallization products on the interface between $\beta\text{-TCP}$ and the glass melt have a significant effect on the strength properties of CM (Table 5).

TABLE 3

Parameter	Glass	
	NS-2A	MTO
Composition, %:		
SiO_2	73.0	73.5
Al_2O_3	3.5	1.5
Na_2O	11.0	15.5
K_2O	2.0	—
CaO	7.0	6.0
MgO	1.0	4.0
B_2O_3	2.5	—
Degree of cohesion	0.45	0.43
Basicity modulus	0.305	0.385
Interval $t_g - t_f, ^\circ\text{C}$	570 – 760	590 – 680

The low crystallization capacity of NS-2A glass powders when sintered without calcium phosphate is determined by a relatively high content of Al_2O_3 , which in this composition lowers the tendency of glasses of the $\text{Na}_2\text{O} - \text{B}_2\text{O}_3 - \text{SiO}_2$ system to liquation, and by the high degree of cohesion of the silicon-oxygen skeleton. Usually a modification of glass composition of the liquating or crystallizing types in the course of sintering leads to increased mechanical strength; however, this is not always true of CM based on glasses. The observed creep destruction of samples which contain over 10% $\beta\text{-TCP}$ is the result of calcium phosphate and SiO_2 , which are inter-granular interlayers of the residual vitreous phase with a non-crystalline structure, gliding along the contact grain boundaries. To ensure the strength of adhesion between the material components, it is necessary to exclude the chemical reaction between them or alter the reaction direction. One should not forget that, first, it is virtually impossible in CM technology to develop a composition whose components are totally indifferent to each other, and second, in most cases, the surface chemical reactions between the filler and the matrix deteriorate the properties of the composite.

TABLE 4

Characteristics	$\beta\text{-Ca}_3(\text{PO}_4)_2$	HA	Glass	CaCO_3
Average size, μm :				
of particles	2	4	7	5
of agglomerates	30	20	23	25
Agglomeration coefficient*	15	5	3.3	5

* Ratio of average agglomerate size to average particle size.

TABLE 5

Method of CM production	Phase composition, wt. %			Strength, MPa		Elasticity modulus, GPa
	glass	HA	β -TCP	bending	compressive	
Liquid sintering of glass powders:						
NS-2A and HA	40 – 90	10 – 60	–	4.7 – 12.6	12.8 – 18.0	1.8 – 5.0
NS-2A and β -TCP	55	35 – 40	5 – 10	1.3 – 2.0	3.1 – 3.9	0.41
MTO and β -TCP	60 – 90	–	10 – 40	4.2 – 7.1	9.9 – 12.2	1.7 – 2.0
Infiltration impregnation of sintered						
HA product with H_3PO_4 solution	50	4 – 40	10 – 46	4.9	11.5	2.0
Sintering of MTO glass, $CaCO_3$, and β -TCP powders	60 – 90	4 – 38	2 – 30	6.9 – 21.1	12.7 – 37.2	2.8 – 8.4

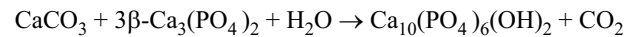
The problem of chemical incompatibility of the filler and the matrix can be solved by replacing the matrix. In our case, only the use of a different glass composition made it possible to obtain biocompatible CM in which the content of β -TCP was brought up to 40%. The use of industrially produced feldspar glass MTO, authorized for medical applications, as the matrix makes it possible to obtain a CM in which the filler is polymineral and is represented simultaneously by two phosphates: β -TCP and HA. In this case, the material was produced by sintering of mechanically mixed phosphate powders and glass.

While the vector of the chemical reactions between components is determined by the nature of these components, the intensity and the specifics of these reactions on the interphase surfaces largely depend on the production technology. A transition from sintering of glass and β -TCP powders to the impregnation of sintered composite material consisting of the glass matrix and HA with specific reactant solutions significantly expands the possibility of modification of the material. The infiltration impregnation and subsequent heat treatment of a sintered intermediate sample induces chemical reactions in the filler, as a consequence of which HA transforms partly or totally into β -TCP. The new β -TCP phase emerges in the existent glass matrix skeleton, whose spatial continuity prevents the disturbance of the mechanical stability of the material, and thus the effect of wetting on the formation of strong cohesion between the composite components is not the deciding factor. This method makes it possible to obtain CM in which the filler is monomineral or polymineral, and thermal treatment in this case does not deteriorate the service properties (Table 6). In contrast to CM produced by sintering, in this case there is no dependence of the composite properties on the content of the emerging β -TCP phase.

TABLE 6

Sample	Phase composition, wt. %			Total porosity, %	Strength, MPa		Volume weight, kg/m ³
	glass	HA	β -TCP		bending	compressive	
Before treatment	50	50	–	58	3.9	9.7	1000
After treatment	50	25	25	62	4.9	11.5	1070

Another method of synthesis of phosphate-bearing CM based on a glass matrix is the combination of liquid sintering of glass and filler powders with chemical reactions between the crystalline filler components, whose end products are HA and (or) β -TCP. The transformation of calcium phosphate in the solid state is characterized by low intensity. For instance, the degree of transformation of β -TCP at 1000°C according to the reaction



does not exceed 12%, which makes it necessary to use higher temperatures, at which calcium phosphates transform into a condensation-crystalline form with a highly ordered structure and extremely low bioactivity. With the glass phase being in the liquid-fluid state, not only the mass transfer processes are intensified, but also Ca^{2+} ions are redistributed between the glass phase melt and the crystalline filler. The glass acts as a sort of buffer, maintaining a certain concentration of Ca^{2+} ions and ensuring their removal from the reaction zone in the case of the formation of intermediate compounds limiting the reaction rate.

Although the presence of interrelated phases satisfies the broad definition of a composite material, the microstructure, properties, and the type of destruction of finished materials with the same phase composition can differ significantly, depending on the production method. In production of material by sintering or impregnation with subsequent heat treatment, the emerging structure should be regarded as two interpenetrating continuous skeletons, one consisting of vacancies, and the other of the glass matrix, whereas the crystalline filler is dispersed on the surface and between the partitions of the glass matrix. When sintering is combined with chemical reaction proceeding inside the filler, the structure represents an assembly of discrete crystalline particles and isolated vacancies dispersed in a continuous glass skeleton.

As the filler content increases, the general trend in the modification of the porous structure of materials made from NS-2A or MTO and HA by sintering consists in a gradual decrease of the total porosity from 78 to 45%, due to agglomeration of small-size pores, which leads to an increased quantity of medium-size and large pores

up to 500 μm . Since perfect wetting in sintering does not exist in this composite, the HA particles are enlarged due to the inability of the liquid melt to penetrate through their whole assembly, which is especially noticeable with a high HA content. This weakens sintering bridges, which are sources of fracture.

In the case of a sintered material made of NS-2A and β -TCP, or a material produced by the combination of chemical reaction in the filler and sintering, the structural destruction starts either inside the matrix, when it reaches the maximum tension, being compressed, or near the surface of the matrix – particle interface, since the melt existing at the sintering temperature fully wets and envelopes solid phase particles, and in doing so, a fully disperse structure with isolated pores (not more than 170 μm) is formed.

The existence of porosity is a necessary condition for using material as a bioactive implant for ingrowth of collagen fibers and blood vessels. Furthermore, it is proved that in a structural-mechanical context, the vacancies have a strong effect on the shear resistance and compressive strength. Porosity, on the one hand, limits the mechanical stability of the material and, on the other hand, acts as a load absorber. The mechanical properties are bounded by the limiting value, which makes it possible to treat the material with a standard surgical instrument. Such treatment, on the one hand, makes it possible to modify the size and shape of a standard implant, taking into account the individual anatomical characteristics of a patient, and, on the other hand, is needed in order to fit the implant to available bone fragments with a degree of precision which determines the evolution of a connective-tissue capsule.

The CM produced by liquid sintering of HA powder and MTO glass powder and their subsequent impregnation with phosphoric acid solution was tested for its capacity for machining with standard surgical tools. Bone samples from an allotransplant of a human skull foramen were used as the reference standard. It was established that the rates of drilling and milling of this material employing milling cutters of various diameters constitute 2.8 – 4.3 mm/sec, which is comparable to the rate of mechanical treatment of bone tissue.

The development of implant CM with preset properties makes it necessary to determine the criteria for the selection of components based on their physicochemical, thermal, mechanical, technological, and other properties. It is possible to distinguish the following classical and specific rules for the development and study of medically utilized composites of the calcium phosphate – glass type:

- the glass composition should not contain toxic components;
- the glass composition should have high chemical stability and should not modify the body liquid pH;
- the glass matrix ensures material continuity upon introduction of the filler in amounts equivalent to the content of calcium phosphate in bone tissues which are replaced by implants;

- the temperature interval for the production of composite material should coincide with the range of thermal stability and biological activity of the filler, namely, calcium phosphate;

- the modification of the porous structure and properties of the material is implemented by varying the mutual position and the quantitative ratio of the composite components, the production method, and its technological parameters;

- the matrix and the filler in the finished material should represent a balanced system for reception, transmission, and absorption of stresses arising in deformation, while preserving mechanical stability;

- the mechanical strength of the composite material is limited, on one side, by the minimum value allowing for implanting and, on the other side, by the maximum values which allow for mechanical treatment of the material employing a standard surgical instrument.

The study of the possible ways of synthesis of CM with a polymineral filler consisting of HA and β -TCP demonstrated that only the methods of thermochemical treatment (with H_3PO_4 solution) of the intermediate product obtained by sintering of HA and β -TCP make it possible to obtain samples with a wide range of β -TCP concentration, sufficient strength, and a permeable porous structure.

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